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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Leino et al.
Serial No.: 09/445,710
Filed: 03/13/2000

Art Unit: 1731
Examiner: Alvo, M

For: PROCESS FOR STABILIZING THE pH OF A PULP SUSPENSION AND FOR PRODUCING PAPER FROM THE STABILIZED PULP

DECLARATION UNDER 37 C.F.R § 1.132

Honorable Commissioner of
Patent and Trademarks
Washington D.C. 20231

I, the undersigned LEINO, Hannu, declare and state that:

I am an inventor of the present US Patent Application.

I have been employed in designing systems for utilizing carbon dioxide in papermaking processes since 1996 in the Finnish company Oy AGA Ab in Espoo, Finland.

I have found that the behaviour of carbon dioxide in papermaking processes is unpredictable and has surprising effects on the alkalinity and stability of pH of a pulp suspension.

This Declaration describes how the AGA Pulp Wash system with CO_2 was applied to improve the pulp washing in the fiber production lines of AssiDomän Skärblacka mill in Sweden. The results of the initial runs are described in an article by Gunilla Östberg et al, and cited as the OSTBERG reference in my US Application 09/445,710. The Declaration also describes how the OSTBERG method differs from using a combination of CO_2 and NaOH in accordance with my invention.

The buffering capacity (alkalinity)

If the pH of a process is insensitive to small additions of acids or bases, it is called a buffered system. This means that the pH is stable.

Equation (1) is the conceptual definition of alkalinity, which is the measure of the buffering capacity of an aqueous system.

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad (1)$$

The alkalinity of an aqueous solution is measured by titrating the sample with a standard acid to an indicator endpoint.

As an example, Figure 4 presents titration curves for four different pulp suspensions having different alkalinity. The better the sample is able to withstand the acid i.e. the more acid is consumed to achieve a certain pH, the better is the buffering capacity. The pulps in Fig. 4 were titrated with H_2SO_4. The pulps having an alkalinity of 5-10 mmol/l give a flat titration curve, which indicates that they provide a stable pH in the papermaking process. The pH of the pulps having low alkalinity (0-0.5 mmol/l) decreased abruptly when acid was added and these pulps are consequently instable in the papermaking process.

AssiDomän Skärblacka mill

Conventional operations at Skärblacka mill prior to the use of CO_2, i.e. without the AGA Pulp Wash system

Fiber line 2

Fig.1 shows the process at Skärblacka mill in fiber line 2 prior to the time when Skärblacka started to use CO_2 according to the AGA Pulp Wash system which is described e.g. in Patent Publication WO 88/04705.

The raw material was cooked in the cooker (1) and washed in the diffuser washer (2). Thereafter the fibers were screened (3) and filtered in the Lindblad filter washers (4) from where the filtrate was returned to the previous washing stages (2) and to the cooking (1). After the filtering the pulp was stored in the storage tower (5). The pulp was then dewatered in the Sunds press (6) to increase the consistency of the pulp to over 30%. The filtrate (water) from the Sunds press (6) was used to dilute the pulp to be pumped from the storage tower (5) to the Sunds press (6).

The pulp which had been dewatered in the Sunds press (6) was refined (7 and 8) in the paper mill. It was diluted with water from the paper mill water circulation (11) for use in the papermaking. Thus, there was a segregation of the water circulations between the fiber plant and the paper mill stock preparation taking place in the Sunds press. This is a common feature in papermaking since the aim is to return as much as possible of the organic and inorganic residual material dissolved in the cooking to the chemical recovery cycle in the fiber plant or alternatively to the waste water treatment. These residuals dissolved in the cooking also interfere with the papermaking at the paper mill. The process conditions in fiber plant and paper mill (pH, chemicals used etc.) are specific to these processes and it is beneficial to keep water exchange at its minimum.

The operations of the fiber line 2 in Skärblacka as described in Fig. 1 had problems with fluctuations of the pH of the pulp, which was fed to the paper mill stock preparation. These pH fluctuations were mainly caused by insufficient dewatering capacity and washing in the Lindblad filter washers (4). This resulted in high carry over in the pulp. With the concept "carry over" in the pulp is meant the organic and inorganic material, which is dissolved in the cooking and which follows the pulp.

The pulp coming from the cooking contained alkali from the alkaline cooking chemicals so the pulp to the paper mill stock preparation was still slightly alkaline. When the pH was too low, Skärblacka mill, in this operation before any CO_2 was used at the mill, charged NaOH to the

aqueous pulp before the Sunds press (6), thus increasing the pH to improve the subsequent refining. The explanation given by OSTBERG (page 515) is that even though a pH lower than 9-9.5 would have been desired "the pH was controlled by addition of alkali, because the pH was easier to control in that way." Thus, the NaOH was added specifically for adjusting the pH.

In the Sunds press (6) the pulp was pressed to a very high consistency (over 30%) meaning that there was no free water present. Since the ions responsible for alkalinity are water-soluble, any such ions would have been substantially removed with the water. Partly due to the high consistency and partly due to the low initial alkalinity in the pulp being pressed, the pulp being fed to the stock preparation of the paper machine had low alkalinity (alkalinity 1-2 mmol/l), which was not sufficient to create a buffering effect in the paper machine (see also Fig. 4).

Fiber line 1

Skärblacka mill had also another fiber line, namely fiber line 1, which was producing bleached pulp. After the cooking the pulp was washed, screened and delignified further with oxygen. After the oxygen delignification, the pulp was washed again before the 4-stage bleaching sequence. The filtrate from the washing was led countercurrently to the previous washing stages and to the cooking.

The pulp contained alkali from the alkaline cooking chemicals and the oxygen delignification chemicals. There were runnability problems in the washers both before and after the oxygen delignification and the insufficient washing caused high carry over in the pulp to the bleaching. Carry over is the dissolved organic and inorganic material following the pulp from the cooking and oxygen delignification. The high carry over in the pulp consumed bleaching chemicals.

After the oxygen delignification the pulp was bleached using chlorine dioxide (ClO_2). The bleached pulp was stored and led to the paper machine stock preparation at about 10-12 % consistency. The pH of the bleached pulp was acidic i.e. pH 4-5. The fiber plant and the paper mill had separate water circulations as usual, meaning that the pulp was picked up from the bleached pulp storage with the paper machine water. The alkalinity of the pulp produced with normal operations had very low alkalinity due to the low pH of the pulp after the bleaching (alkalinity 0-1 mmol/l).

Operations with the AGA Pulp Wash system using CO_2

Fiber line 2

Fig. 2 shows the operation of the fiber line 2 when the AGA Pulp Wash system described by OSTBERG was taken into use. As seen in Fig. 2, CO_2 was added to the pulp stream going to the screening (3). The pH of the pulp was lowered to about 8.5 with CO_2 and the washing result in the Lindblad filter washers (4) was improved.

When CO_2 according to the AGA Pulp Wash had been taken into use, the washing performance of the Lindblad filter washers improved and was stabilized. This resulted in a more stable pH of the pulp leaving the fiber plant. When the pH fluctuations disappeared, the need for adjusting the pH disappeared. When the pH was stable at about 8, there was no addition of NaOH to the pulp as indicated in Fig. 2. The CO_2-charge was 3 kg CO_2/t pulp to the washing.

Pulp produced with the AGA Pulp Wash system leaving the fiber plant had low alkalinity (2-3 mmol/l). This is due to the segregation of water circulations between the fiber plant and the paper mill by the Sunds press and due to the small amount of bicarbonate created by the AGA

Pulp Wash system. With the AGA Pulp Wash System using CO_2 the increase in the alkalinity (bicarbonate content, see equation 1) is about 3 mmol/l. However the major part of the bicarbonates follows the filtrates back to the cooking because the washing filtrates are used countercurrently in the fiber plant.

The water circulations in the fiber plant and the paper machine are separated in the Sunds press (6) where the pulp is pressed from the consistency of about 14% to over 30 %. Already in the Lindblad filters (4) the consistency is increased from 4% to 14%. This means that at most a third of the alkalinity created by CO_2 follows the pulp to the paper machine stock preparation (i.e. 1 mmol/l). In the paper machine stock preparation after the Sunds press the pulp is gradually diluted to 1 % consistency with the paper machine waters (11) so the alkalinity created by CO_2 in the fiber plant is negligible in the stock preparation of the paper mill i.e. has no practical significance.

Fiber line 1

In the fiber line 1 at Skärblacka producing bleached pulp, CO_2 was charged at washing in three different positions before the 4-stage bleaching sequence:

- at the end of the Ultrawasher 1 (after cooking)
- at the end of the Ultrawasher 2 (after O_2 delignification)
- at the blow tank after the O_2 delignification stage

With CO_2 the pH was decreased in the washers and, as a result, the drainability (dewatering) improved on the Ultrawashers and on the filter washer. In the Ultrawasher 2 before the bleaching sequence the pH was decreased to below pH 9.5. The total CO_2 charge was 3-4 kg CO_2/t pulp. The bleaching was performed the same way as before so the pH of the bleached pulp was acidic i.e. pH 4-5. The fiber plant and the paper mill had separate water circulations as usual meaning that the pulp was picked up from the bleached pulp storage with the paper machine water. The alkalinity of the pulp produced with the AGA Pulp Wash system was the same as that of the pulp produced with conventional operations i.e. very low (alkalinity 0-1 mmol/l).

AssiDomän Skärblacka is presently using the AGA Pulp Wash system in their both fiber lines, so I am well informed of the process conditions.

Operations when using my invention called ADALKA (a combination of CO_2 and NaOH)

The method according to the present Application Ser. No 09/445,710 (the so called ADALKA process) is presently in use e.g. in the UPM-Kymmene Kymi Paper mill in Finland. UPM-Kymmene is one of the biggest pulp and paper companies in the world having production plants world-wide. The ADALKA process is not in use at Skärblacka mill. However, for the sake of ease of understanding, I have transported the ADALKA operations from the Kymi Paper mill to Fig. 1 describing fiber line 2 of Skärblacka. Thus, enclosed Fig. 3 shows fiber line 2 and the stock preparation of Skärblacka's paper machine No. 9 as if the ADALKA process were in use there. Paper machine No. 9 uses unbleached pulp produced in fiber line 2.

As seen in Fig 3, the water circulations of the fiber plant and the paper mill have been segregated after the Sunds press (6). This makes it possible to increase the alkalinity of the pulp suspension in the stock preparation of the paper machine without affecting the pH adjustments required in the fiber line. A combination of CO_2 and NaOH is charged to the pulp suspension in the stock preparation in accordance with my invention. There is hardly any need to adjust the pH of the pulp, since the pH is close to the desired value as it is. The aim of adding the two

chemicals CO_2 and NaOH in my invention is not pH adjustment as such. The aim is to increase the buffering capacity of the pulp in order to stabilize the pH throughout the papermaking. An improved pH stability is obtained by the resulting increase in the alkalinity of the pulp suspension in the stock preparation of the paper machine.

In the paper machine stock preparation of Fig. 3 the buffering capacity measured as alkalinity is increased by the ADALKA process to 8-12 mmol/l by adding about 3-8 kg CO_2/ton pulp in combination with about 3-8 kg NaOH/ton pulp. The alkalinity increases in the pulp suspension throughout the papermaking (refining, machine chest, mixing chest, headbox, etc.) and in the paper machine water circulation (wire pit, clear filtrate, etc) i.e. also in the water which is used to dilute the pulp in different positions in the paper machine stock preparation. At need the pH of the pulp is adjusted to a desired level by controlling the ratio of CO_2/NaOH.

Fig. 3 describes the use of ADALKA for unbleached pulp. ADALKA may also be applied to Skärblacka's paper machine No. 8 which uses the bleached pulp produced at the fiber line 1. The pH of the pulp in fiber line 1 after the bleaching is so low that the alkalinity is practically 0 mmol/l when fed to the paper machine. When my invention (ADALKA) is taken into use, the combination of CO_2 and NaOH is added to the pulp suspension after the bleaching when the pulp is fed to the paper machine to increase the alkalinity e.g. to 8-12 mmol/l. The increased alkalinity keeps the pH of the pulp stable throughout the subsequent papermaking process.

The above indicates very clearly that the alkalinity obtainable by the process described by OSTBERG creates an alkalinity of about 0 to 1 mmol/l which is not sufficient to stabilize the pH of the pulp as seen in Fig. 4. In sharp contrast to this, the high alkalinity obtained with my invention ADALKA provides a substantially increased stability and hence an improved papermaking process.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that all these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed in Espoo, Finland, on December 20, 2002

Hannu Leino